

# Binary Alloy Phase Diagrams

## Second Edition

### Volume 2

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The output of the International Data Program for Alloy Phase Diagrams, including the "Program" phase diagram evaluations contained in this compilation, has been reviewed by the Office of Standard Reference Data and accepted as a product of the National Standard Reference Data System.



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### Cu-Rh, Cu-Ru, Cu-S

ments were made, the liquidus was not determined.

The Cu-Rh system is characterized by the presence of an isomorphous solid across the entire diagram in the temperature regions immediately below the solidus. The solidus determined by the incipient fusion technique appears nearly flat between approximately 25 and 50 at.% Rh. This would imply a shallow free-energy versus composition curve of the solid in corresponding composition and temperature ranges and a tendency toward formation of a miscibility gap at lower temperatures.

A single-phase continuous solid solution field exists between the components below the solidus. At still

lower temperatures, the phase field enters into a wide miscibility gap wherein it separates into two equilibrium isostructural phases, one of which is rich in Cu and the other in Rh. The critical temperature and composition of the gap are 1150 °C and 60 at.% Rh, according to [71Rau].

The miscibility gap boundary given by [71Rau] has been modified slightly in this evaluation in order to include, inside the gap, the compositions for which the X-ray showed a two-phase structure. The gap boundaries at 800 °C, according to [71Rau], are approximately at 25 and 90 at.% Rh.

The existence of a metastable single-phase continuous solid solution be-

tween (Cu) and (Rh) was established by [64Luo], based on rapid solidification of the alloys from the melt. This is in agreement with the generally accepted conditions for mutual solubility of metals in the solid state, which Cu and Rh satisfy. Transition to equilibrium phases occurred when the samples were heated at 600 °C for seven to ten days.

64Luo: H.L. Luo and P. Duwez, *J. Less-Common Met.*, 6, 248-249 (1964).

71Rau Ch.J. Raub, E. Röschel, D. Menzel, and M. Gadhol, *Metall.*, 25(7), 761-762 (1971).

Published in *Bull. Alloy Phase Diagrams*, 2(4), Mar 1982. Complete evaluation contains 1 figure, 2 tables, and 10 references.

## Cu-Ru (Copper-Ruthenium)

P.R. Subramanian and D.E. Laughlin

 Experimental data on the Cu-Ru system are very limited. Electrical resistivity measurements showed negligible solid solubility of Ru in (Cu) at 900 °C [32Lin]. There are no other reports on the Cu-Ru system.

The equilibrium phases of the assessed phase diagram are: (1) the liquid, L; (2) the fcc terminal solid solution, (Cu), with very limited solid solubility of Ru; and (3) the cph terminal solid solution, (Ru), with very limited solid solubility of Cu. The as-

### Cu-Ru Crystal Structure Data

| Phase     | Composition<br>at.% Ru | Pearson<br>symbol | Space<br>group       | Struktur-<br>bericht<br>designation | Prototype |
|-----------|------------------------|-------------------|----------------------|-------------------------------------|-----------|
| (Cu)..... | 0                      | cF4               | Fm $\bar{3}m$        | A1                                  | Cu        |
| (Ru)..... | 100                    | hP2               | P6 <sub>3</sub> /mmc | A3                                  | Mg        |

essed diagram is schematic, because it is based on a simple thermodynamic model [83Nis].

32Lin: J.O. Linde, *Ann. Physik.*, 15, 219-248 (1932) in German.

83Nis: A.K. Niessen, F.R. de Boer, R. Boom,

P.F. de Chatel, W.C.M. Mattens, and A.R. Miedema, *Calphad*, 7(1), 51-70 (1983).

Submitted to the APD Program. Complete evaluation contains 1 figure, 2 tables, and 4 references.

## Cu-S (Copper-Sulfur)

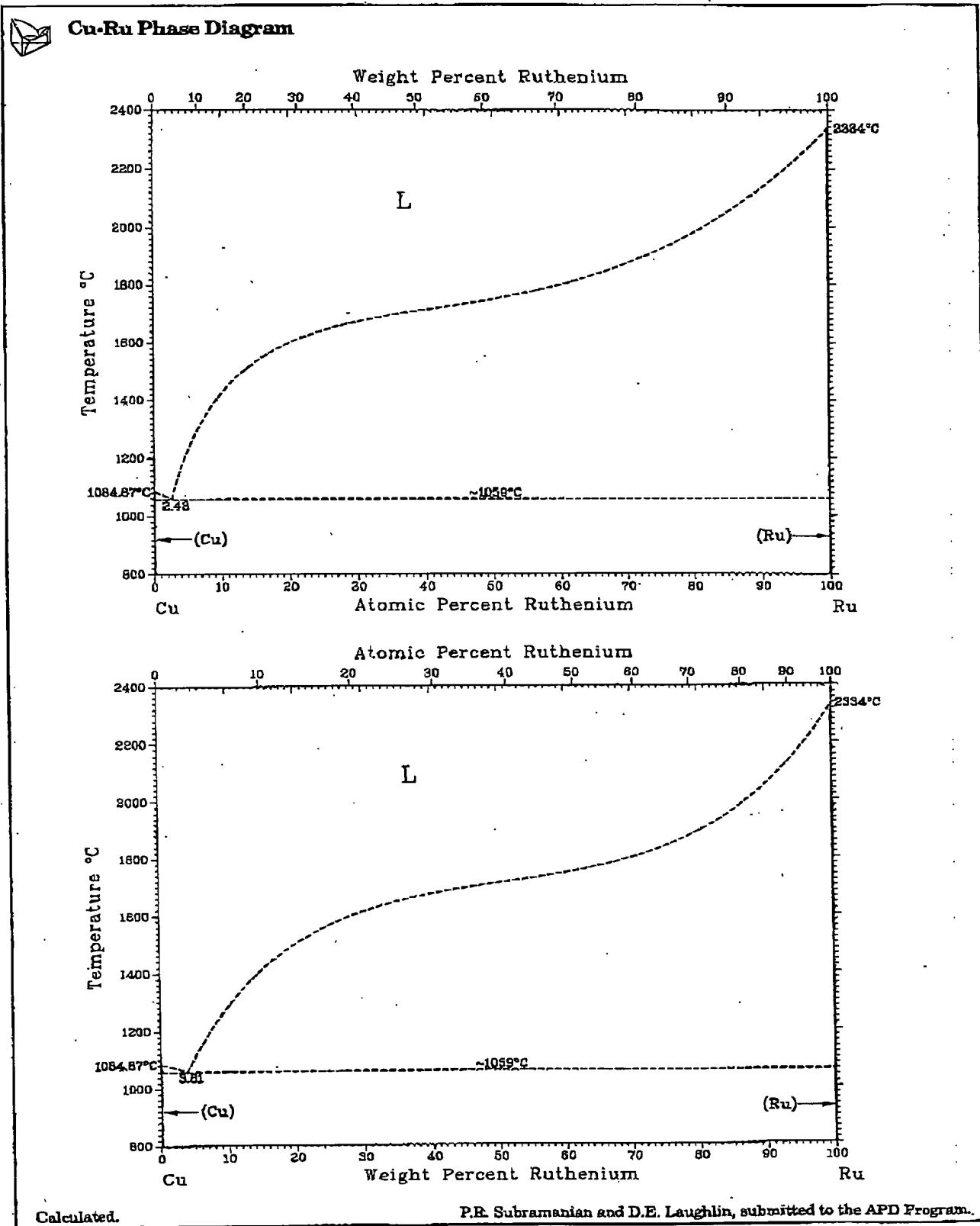
D.J. Chakrabarti and D.E. Laughlin

 Numerous studies have been conducted on the Cu-S system. Uncertainty, however, persists regarding the phase equilibria, because of the strong tendency of the sys-

tem to form several metastable phases. Marked thermomechanical history dependence is exhibited by many of these phases. For example, extreme sensitivity to applied pressure has been

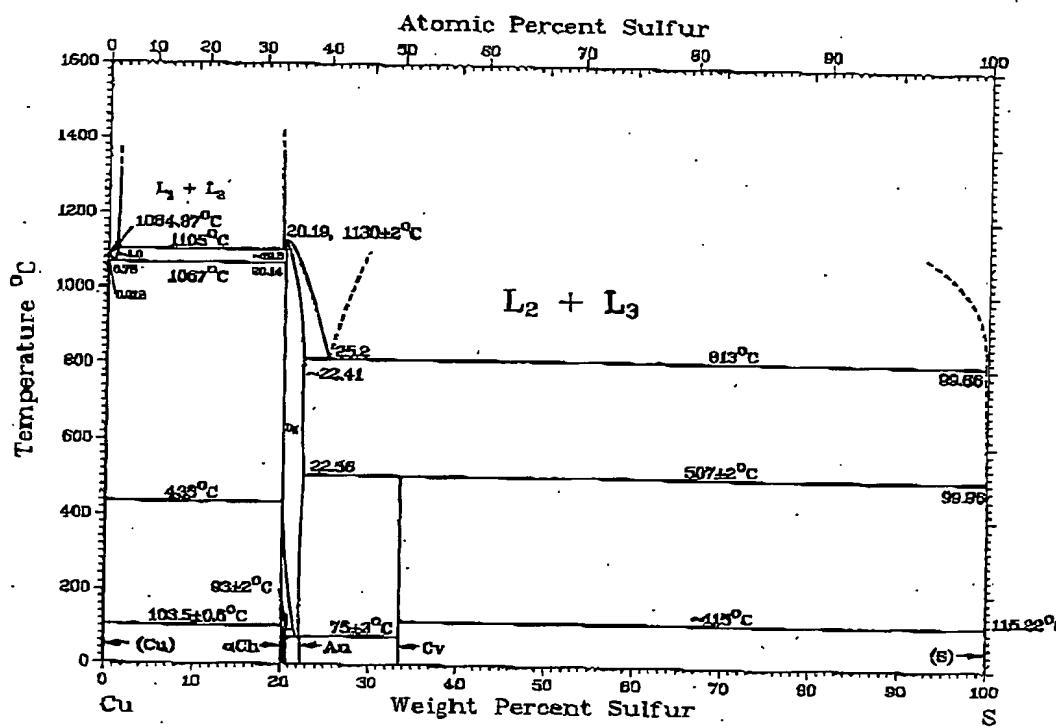
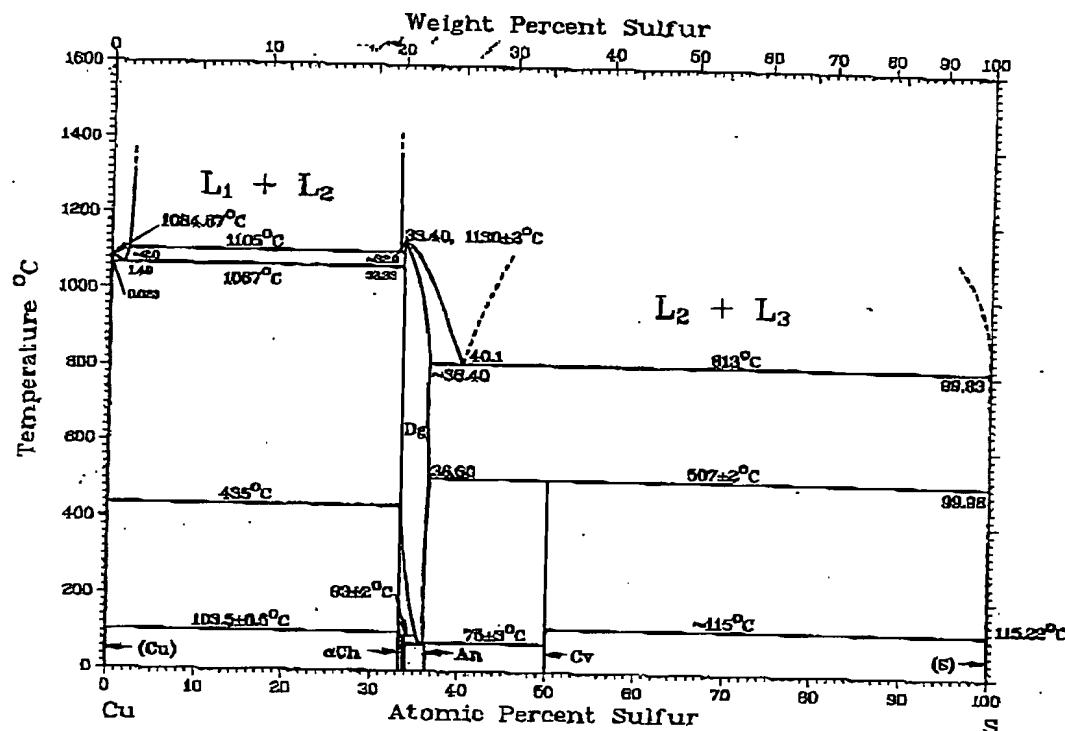
known to cause a phase transformation during specimen preparation by grinding.

However, the following features have been well established. The liquid, L,

**Cu-Ru**

## Cu-S

Cu-S Phase Diagram



Compositions in parentheses are calculated values by [80Shal].

D.J. Chakrabarti and D.E. Laughlin, 1983.

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**Cu-S**

manifests two miscibility gaps between the liquids L<sub>1</sub> and L<sub>2</sub> above 1105 °C at Cu-rich compositions and between the liquids L<sub>2</sub> and L<sub>3</sub> above 813 °C at higher S compositions. The fcc terminal solid solution, (Cu), exhibits restricted solubility of S, amounting to 0.028 at.% at 1067 °C. The solubility of S decreases with increasing purity of Cu. The orthorhombic terminal solid solution, (S), is stable up to ~115 °C, with negligible solubility of Cu.

The monoclinic low-chalcocite ( $\alpha$ Ch), is stable up to  $103.5 \pm 0.5$  °C at the stoichiometric composition of Cu<sub>2</sub>S and up to  $90 \pm 2$  °C at 33.41 at.% S. The hexagonal high-chalcocite ( $\beta$ Ch) is stable from  $103.5 \pm 0.5$  °C at the Cu-rich limit of stoichiometric Cu<sub>2</sub>S and from  $90 \pm 2$  °C at 33.44 at.% S up to 485 °C at 33.34 at.% S.

The fcc digenite (Dg) has a broad phase field, with the Cu-rich boundary approximately at Cu<sub>2</sub>S stoichiometry

between 435 and  $1130 \pm 2$  °C. The Cu-deficient boundary extends to form the defect compound Cu<sub>2-x</sub>S, which is stable up to  $507 \pm 2$  °C at 36.60 at.% S and down to  $72 \pm 8$  °C at 35.65 at.% S.

The orthorhombic djurleite (Dj) has the nominal composition Cu<sub>1.96</sub>S and is stable up to  $72 \pm 3$  °C at Cu<sub>1.984</sub>S and up to  $98 \pm 2$  °C at 33.99 at.% S. The orthorhombic compound anilite (An) of stoichiometry Cu<sub>1.75</sub>S (36.36 at.% S) is stable up to 75 ± 8 °C. The hexagonal

**Special Points of the Cu-S System**

| Reaction                             | Composition,<br>at.% S(Cu/S) | Temper-<br>ature,<br>°C | Reaction<br>type |
|--------------------------------------|------------------------------|-------------------------|------------------|
| L ↔ Dg                               | (1.994)                      | 33.40                   |                  |
| L <sub>2</sub> ↔ L <sub>1</sub> + Dg | 32.9                         | -2.0                    | (2.002)          |
| L ↔ (Cu) + Dg                        | 1.48                         | 0.0225                  | (2.00025)        |
| L <sub>2</sub> ↔ Dg + L <sub>3</sub> | 40.09                        | -85.4                   | 99.83            |
| (Cu) + $\beta$ Ch ↔ $\alpha$ Ch      | -0                           | -33.33 ± 0.02           | -33.33 ± 0.02    |
| $\beta$ Ch ↔ $\alpha$ Ch + Dj        | 33.44 ± 0.06                 | 33.41 ± 0.02            | 32.78 ± 0.02     |
| (Cu) + Dg ↔ $\beta$ Ch               | -0                           | 33.344                  | 33.340           |
| Dg ↔ Dj + An                         | 35.65 ± 0.09                 | 34.08 ± 0.02            | 36.86 ± 0.04     |
| $\beta$ Ch + Dg ↔ Dj                 | 33.47 ± 0.05                 | 35.29 ± 0.03            | 33.99 ± 0.02     |
| Dg + Cv ↔ An                         | 36.17 ± 0.02                 | 50.00 ± 0.02            | 36.36 ± 0.04     |
| Dg + L ↔ Cv                          | 36.60 ± 0.07                 | 99.98                   | 50.00 ± 0.02     |
| L ↔ Cv + (S)/L + Cv ↔ (S)            | -100                         | 50                      | -100             |
|                                      |                              |                         | -115             |

(a) From [72Cool]. (b) From [Hansen]. (c) From [80Joh]. (d) From [47Jen]. (e) From [74Rau]. (f) From [77Pot]. (g) From [66Ros].

**Cu-S Crystal Structure Data**

| Phase   | Composition,<br>at.% S(Cu/S)       | Pearson<br>symbol | Space<br>group                   | Struktur-<br>bericht<br>designation | Prototype         |
|---|------------------------------------|-------------------|----------------------------------|-------------------------------------|-------------------|
| (Cu)  | -0                                 | cF4               | Fm $\bar{3}m$                    | A1                                  | Cu                |
| $\alpha$ chalcocite ( $\alpha$ Cu <sub>2</sub> S) | -33.33                             | mP144(?)          | P2 <sub>1</sub> /c               | ...                                 | ...               |
| $\beta$ chalcocite ( $\beta$ Cu <sub>2</sub> S)   | -32.8                              | hP6               | P6 <sub>3</sub> /mmc             | B82                                 | InNi <sub>2</sub> |
| Djurleite (Cu <sub>1.96</sub> S)                  | 33.7 to 34.1(a)                    | aPS80(?)          | Pmnmm                            | ...                                 | ...               |
|   |                                    |                   | P2 <sub>1</sub> nm(?)            |                                     |                   |
|   |                                    |                   | Pmn21                            |                                     |                   |
| Digenite (Cu <sub>2-x</sub> S)                    | 35.5 to 36.2(b)                    | cF12              | Fm $\bar{3}m$                    | C1                                  | CaF <sub>2</sub>  |
| Anilite (Cu <sub>1.75</sub> S)                    | 36.86 ± 0.04                       | aP44(?)           | Pnma                             | ...                                 | ...               |
| Covellite (CuS)                                   | 50                                 | hP12              | P6 <sub>3</sub> /mmc             | B18                                 | CuS               |
| (S)   | -100                               | aF128             | Fddd                             | A16                                 | $\alpha$ S        |
|   |                                    | mP48              | P2 <sub>1</sub> /a               | ...                                 | $\beta$ S         |
|   |                                    | hR6               | R3                               | ...                                 | $\epsilon$ S      |
| <b>Metastable phases</b>                          |                                    |                   |                                  |                                     |                   |
| Protodjurleite                                    | 33.7 (1.97)(c)<br>33.8 (1.96)(d)   | ...               | ...                              | ...                                 | ...               |
| Tetragonal  | 33.8 (1.96)                        | tP12              | P4 <sub>3</sub> 2 <sub>1</sub> 3 | ...                                 | Ge III(HP)        |
| Hexagonal-tetragonal Cu <sub>2</sub> S            | 34.1 to 36.4 (1.92 to 1.75)        | ...               | ...                              | ...                                 | ...               |
| Low digenite (oDg)                                | 35.84 to 36.15 (1.790 to 1.766)(e) | ...               | R <sub>3</sub> m                 | ...                                 | ...               |
| Blaubleibender covellite I                        | 41.7 ± 1.7 (1.4 ± 0.1)             | ...               | ...                              | ...                                 | ...               |
| Blaubleibender covellite II                       | 47.7 ± 2.3 (1.1 ± 0.1)             | ...               | ...                              | ...                                 | ...               |
| CuS <sub>2</sub>                                  | 56.67 (0.5)                        | ...               | PaS(?)                           | ...                                 | ...               |

(a) At 72 °C. (b) At 80 °C. (c) At 75 °C. (d) At 93 °C. (e) At 25 °C.

